

Dispersive solid-phase extraction followed by liquid-liquid microextraction for extraction and preconcentration of PBDEs from sediment samples prior gas chromatography-mass spectrometry

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Introduction

PBDEs are one of the brominated flame retardants used to protect potentially flammable materials by increasing the resistance to ignition and delaying the spread of fire (Birnbaum and Staskal, 2004, Rahman et al., 2001). PBDEs are additives of polymeric material and, thus are not chemically bound to the chemical structure. Therefore, they may leach from the surface of their product into the environment (de Wit, 2002, de Wit et al., 2006, Stapleton and Dodder, 2008). PBDEs are persistent, have low water solubility and high affinity to suspended particles, which favors their bioaccumulation in hydrophobic mediums of the biota such as sediments (de Wit, 2002). Sediment is one of the major sink to PBDEs in the aquatic environment. Since contaminants can be bioavailable in sediment to different aquatic organisms, the study of sediment is an important stage in tracing possible exposure route to aquatic biota (Yusà et al., 2006). The analysis of sediment samples for PBDEs determination requires highly efficient extraction techniques because the analytes tend to be very strongly bound to the sample matrix. Furthermore, due to the low concentration of the target analytes in sediment samples, it is necessary to count on highly efficient preconcentration techniques for their determination.

In the last ten years, the development of robust analytical methodologies to quantify PBDEs in environmental matrices has reported a rapid growth. Several analytical approaches for both sample preparation and instrumental analysis have been proposed (Covaci et al., 2007, D'Silva et al., 2004). Room temperature lixiviation is an alternative for extracting PBDEs from sediment samples. It can be assisted by auxiliary energies such as ultrasonic (US) radiation in order to favor the kinetic of the mass-transfer process of the target analytes to the liquid phase. It leads to an increment in the extraction efficiency of the technique in a minimum amount of time (Luque de Castro and Priego-Capote, 2006, Luque de Castro and Priego-Capote, 2007). Thus, it turns into an ultrasound assisted leaching (USAL) technique. Due to the low concentration of PBDEs in sediment samples it is necessary to apply a preconcentration technique prior to their GC–MS/MS determination. Recently, a novel microextraction technique, dispersive liquid-liquid microextraction (DLLME), have been reported (Rezaee et al., 2006). DLLME uses an extraction solvent mixture including a high-density non-polar water immiscible solvent (extraction solvent) and a polar water miscible solvent (disperser solvent). DLLME have high preconcentration capabilities in a very short time. The main disadvantage of the DLLME is that it is not a selective extraction technique and also fails if phases do not separate even after centrifugation (in the case of heavily contaminated extracts). Thus, in order to overcome

this problem it is necessary to include a clean-up stage after the analyte leaching from the sample and previous to DLLME technique. Dispersive solid-phase extraction (DSPE) was recently introduced as a rapid and simple technique for clean-up crude extracts of different matrixes (Anastassiades et al., 2003). It is based on the addition of the sorbent material into the extract to remove the matrix co-extractives, which is then separated from the extract bulk by centrifugation. The use of DSPE after USAL would increase the extraction efficiency of DLLME technique and extend its applicability to sediment samples.

The purpose of the present work is to develop a new analytical methodology based on DSPE-DLLME, and demonstrate its applicability for extraction and preconcentration of PBDEs from sediment samples prior their determination by GC–MS/MS. To this aim, four of the most commonly found PBDEs in sediment samples were selected as target analytes: 2,2',4,4'- tetrabromodiphenyl ether (BDE-47), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), 2,2',4,4',6-pentabromodiphenyl ether (BDE-100), 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153). The influence of several variables on the performance of the analytical methodology were studied and optimized over the analytical response of the PBDEs. The analytical performance of DSPE-DLLME-GC–MS/MS methodology was evaluated in terms of method detection limits (MDLs), repeatability and linear working range.

Materials and Methods

The standards of polybrominated diphenyl ethers were purchased from Accustandard (New Haven, CT, USA) at 50 mg L⁻¹ in isooctane and consisted of: 2,2',4,4'- tetrabromodiphenyl ether (BDE-47), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), 2,2',4,4',6-pentabromodiphenyl ether (BDE-100), 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153). Decachloro biphenyl (PCB-209) was used as internal standard (IS). All other reagents used for method development were analytical grade or above.

GC–MS analyses were performed on a Varian 3900 gas chromatograph equipped with Varian Saturn 2000 ion trap mass detector. The system was operated by Saturn GC–MS WorkStation v6.4.1 software. The GC column used was VF-5ms (25m×0.25 mm, 0.25µm film thickness). The oven temperature program was: 150°C, held 1 min; rating 15°C min⁻¹ to 250°C; rating 10°C min⁻¹ to a final temperature of 300°C and held for 7 min. Helium (purity 99,999%) was used as a carrier gas at 1.0 mL min⁻¹ flow rate. The injector temperature was set at 300°C and the injections were performed in the splitless mode. The peak identification was based on the base peak and the isotopic pattern of the PBDEs congeners. Peak identification and quantification were performed against PCB-209 internal standard. A 40 kHz and 600W US-bath with temperature control (Test Lab, Buenos Aires, Argentina) was used for assisting the ultrasound leaching process. Injections into the GC–MS were made by using a 5.0-µL Hamilton syringe.

Sampling and sample preparation

River and lake sediments were analyzed within this study. Two river sediments were collected at different locations of Mendoza River, upstream and downstream to Potrerillos Lake and a third sample was collected in Mendoza city. After collection, samples were dried at 60 °C for 72 h. Dried sediment samples were homogenized using a porcelain mortar and sieved through a 0.3-mm stainless steel sieve. Dried samples were stored in amber bottles in the darkness at room temperature until analysis. The sediment samples used for method optimization were previously analyzed for the compounds of interest and none of the studied analytes was detected. These samples were then spiked with the target PBDEs using methanolic solutions and homogenized as described by Salgado-Petinal et al.

(Salgado-Petinal et al., 2006).
DSPE-DLLME procedure

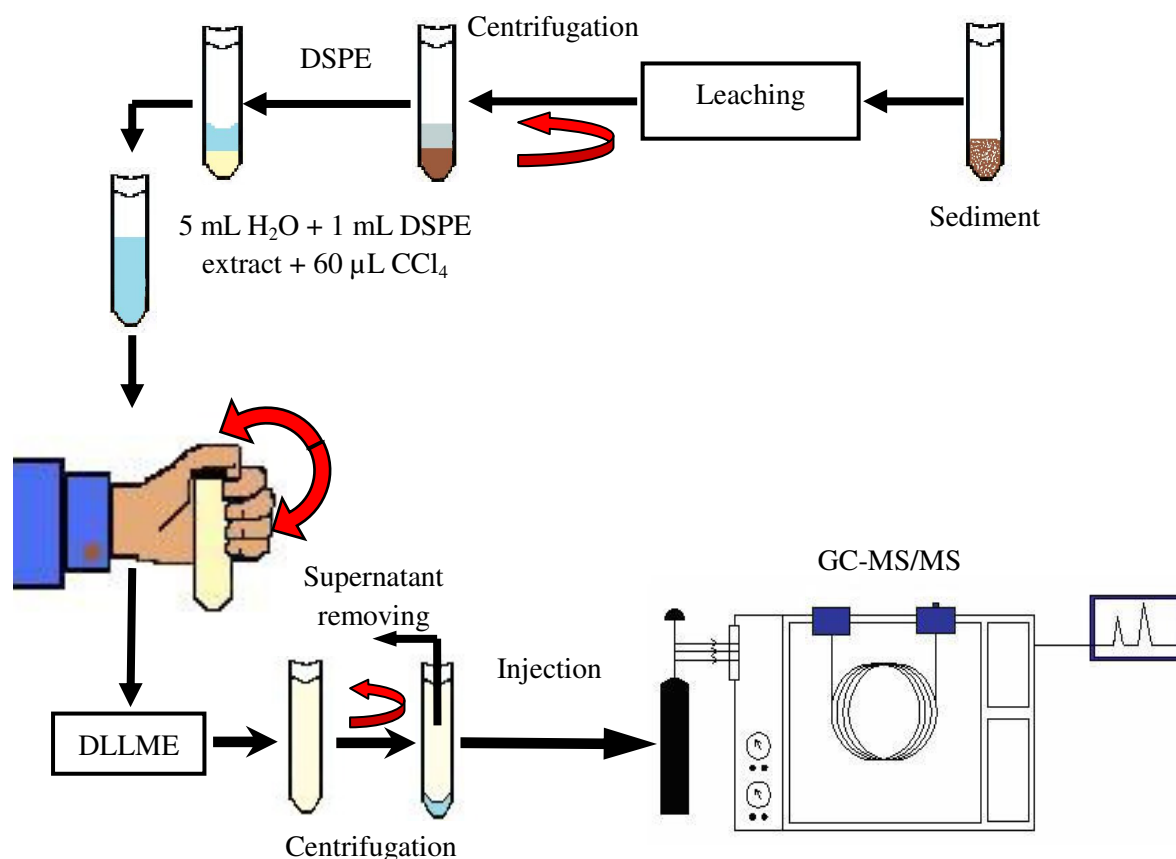


Figure 1 show a schematic diagram of the extraction and preconcentration system.

Results and Discussion

Leaching the analytes from the sample provides a cleaner liquid extracts since some matrix interferences remain in the sediment (Luque de Castro and Priego-Capote, 2006). However, this extract still might contain some matrix concomitants that could interfere in the preconcentration technique. Therefore it is necessary to include a clean-up step after leaching in order to overcome the mentioned analytical inconvenient. Several critical variables were studied and optimized in order to achieve an efficient DSPE clean-up. The main ones were leaching solvent type and volume, ultrasonication time and mode, leaching temperature and sorbent type used for DSPE.

After DSPE clean-up, an acetone extract containing the target PBDEs was obtained. DLLME was chosen for such purpose. The extraction efficiency of DLLME technique can be affected by different variables including extraction solvent type and volume, extraction temperature and time, medium ionic strength and disperser solvent. In this case, the disperser solvent was fixed by the previous stage, and was acetone. The study and optimization of the above mentioned variables were performed by modifying one at a time while keeping the remaining constant.

Under optimum conditions, the methodology detection limits (MDLs) of PBDEs calculated as three times the signal-to-noise ratio (S/N) were within the range 0.02 – 0.06 ng g⁻¹. The relative standard deviations (RSDs) for 5 replicates were < 9.8 %. The calibration graphs were linear within the concentration range of 0.07-1000 ng g⁻¹ for BDE-47, 0.09-1000 ng g⁻¹ for BDE-100, 0.10-1000 ng g⁻¹ for BDE-99 and 0.19-1000 ng g⁻¹ for BDE-153 and the coefficients of estimation were ≥0.9991. Validation of the methodology was performed by standard addition method at two concentration levels (1 and 20 ng g⁻¹). Recovery values were ≥80 %, which showed a successful robustness of the analytical methodology.

The proposed preparative technique based on DSPE-DLLME is an efficient extraction and preconcentration alternative for PBDEs determination at trace levels in sediment samples. The combination of leaching-DSPE led to an enhancement of selectivity and sensitivity of the methodology; and supports the DLLME preconcentration capabilities to complex sediment matrices. Under optimized working conditions, MDLs were in the order of picogram per gram suitable for real world applications with an acceptable precision. DSPE-DLLME used simple and inexpensive equipment and so it is applicable for most of the analytical laboratories. Furthermore, the developed DSPE-DLLME provides good linearity, precision and quantitative recoveries. The proposed methodology has been applied for the extraction, preconcentration and determination of PBDEs in real sediment samples with satisfactory robustness. DSPE-DLLME-GC-MS/MS analysis is appropriate as a potential methodology in routine analysis to determine trace levels of PBDEs in environmental sediments due to their simplicity, ruggedness and cost/effectiveness ratio.

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